5-1946

A Preliminary Investigation of the Hydrometallurgy of Philipsburg Manganese

W. L. Goodman

A PRELIMINARY INVESTIGATION OF THE HYDROMETALLURGY OF PHILIPSBURG MANGANESE

A Thesis

Presented to

the Department of Metallurgy

Montana School of Mines

In Partial Fulfillment

of the Requirements for the Degree

of Bachelor of Science

---

by

W. L. Goodman

May 1946

A PRELIMINARY INVESTIGATION OF THE HYDROMETALLURGY OF PHILIPSBURG MANGANESE

A Thesis

Presented to

the Department of Metallurgy

Montana School of Mines

In Partial Fulfillment

of the Requirements for the Degree

of Bachelor of Science

by

W. L. Goodman

May 1946

TABLE OF CONTENTS

	Page
Introduction	1
Acceptability of Electrolytic Manganese to the Steel Industry	5
Previous Investigations	7
Montana's Position in National Production of Manganese	10
Leaching Experimental Work	11
Test No. 1 - (Preliminary Test)	12
Test No. 2 - Solubility of sample in various concentrations of sulphuric acid	14
Test No. 3 - Determination of the consumption of SO_2	16
Test No. 4 - Determination of the effectiveness of thedegree of acidity of the solution in sulphuric acid with different strengths of sulphurous acid	18
Test No. 5 - To determine if the added recovery indicated in the previous test is consistent with varying concentrations of SO_2 solution	21
Test No. 6 - To determine the effect of the time of leach upon recovery ...	23
Conclusions	26
Recommendations for Further Investigation	28
Bibliography	29
Acknowledgment	30
Tables (Index)	ii
Graphs (Index)	iii

TABLES

Table		Page
1.	Solubility of Sample in Various Concentrations of H_2SO_4	14
2.	Consumption of SO_2 for Recovery of Manganese	16
3.	Effectiveness of Concentration of Sulphuric Acid in the Leach upon the Recovery of Manganese	18
4.	Recovery of Manganese with optimum H_2SO_4 acidity	21
5.	Effect of Time of Leach upon Recovery of Manganese with Different H_2SO_4 acidity	23

GRAPHS

Plate		Page
1.	Recovery of Manganese with Various Concentrations of H_2SO_3 and H_2SO_4	19
2.	Recovery of Manganese with Various Strengths of Acidity	22
3.	Recovery of Manganese with Various H_2SO_4 Acidity and Time of Leach	24

INTRODUCTION

Manganese being essential in the manufacture of steel, the insuring of an adequate supply is imperative. By present practice every long ton of steel produced requires the equivalent of about 14 pounds of metallic manganese. The 1941 needs for ferro-manganese (78 - 82 % Mn) was 1,260,000 long tons, while normal requirements amount to approximately 1,000,000 long tons. In the past the steel industry of the United States has depended almost wholly on imports for its supplies of manganese. Although it is well known that there are enormous deposits of low grade manganese ore in the United States the production of substantial amounts of ferro-grade material from domestic sources presents a field for constructive and practical research.

In spite of the definite advances in milling manganese ores, many ores will not yield a high recovery of ferro-grade concentrate by present milling methods -- if the mineral is largely pyrolusite, crushing produces an excessive proportion of slimes difficult to recover by gravity separation. Also there is a great volume of ores in which the manganese minerals and the gangue are so intimately associated that separation requires some hydrometallurgical or or pyrometallurgical process. In order to interpret

properly the possibility of concentrating at a profit any type of manganese bearing material, many technical and economic factors must be considered.

The exhaustive investigation of the manganese-ore deposits of this country, which has been carried out since 1938 by the Bureau of Mines, has not revealed great amounts of ore suitable for furnace treatment but it has revealed large amounts of ore suitable either directly or indirectly for making electrolytic manganese (greater than 110,000,000 tons).

As stated by C. K. Leith, former member of the War Production Board [1**]

> "The United States has important low-grade ore reserves which are likely to become available by improvements in the technology of extraction. Such an industry is a far stronger support in a national emergency than units of raw material held back for such emergency by restriction of production. It is important that processes and projects for the use of low-grade ores be encouraged, not only for war preparedness but for our industrial future."

The following types of manganese ores should be considered from the standpoint of hydrometallurgy:

1. Those that are not amenable to a satisfactory concentration. These constitute the main field because of the enormous quantities of low-grade ore which are at present useless.

2. Those manganese ores containing precious metals (Au & Ag)[2]

> "Gold and silver from the standpoint of the steel manufacturer has no value. In some ores the silver content is such that the ore

** All references listed in Bibliography.

has greater value for the lead smelter. The manganese then acts as a flux and the silver may be recovered by purification of the lead."

Such ores could first be treated for manganese and the residue may then be amenable to cyanidation for the recovery of Au & Ag. (The presence of oxides of manganese interfere with the cyanidation of Au & Ag).

Quoting C. W. Davis - United States Bureau of Mines [3]

"The value of a hydrometallurgical process for manganese depends on the present and future uses for manganese products. The greater part of manganese consumed at present goes into the manufacture of iron and steel. One can hardly expect hydrometallurgy to compete on an equal footing for this use, but in the case of curtailed supplies of suitable manganese ores the importance of a stand-by process is evident. There are however many other important industries for which hydrometallurgy processes might hope to furnish the supply of manganese or its compounds -- electric batteries, manufacture of glass, pottery, tile, paint, ink, textiles, fertilizers, and manganese alloys."

(The use of manganese sulphate as a fertilizer has been shown by years of experience to be helpful as a crop stimulant. The probable future use of manganese sulphate as a fertilizer will consume a considerable tonnage of manganese. This production depends entirely on hydrometallurgy).

The high cost of dissolving the manganese mineral and the recent progress in development of a commercial method for the production of electrolytic manganese favor the preparation of high grade electrolytic manganese.

The production of electrolytic manganese is of considerable importance in industry for the pure material produced by this process enables a close control of alloys that is otherwise impossible.[4]

> "Electrolytic manganese produced is 99.95 percent or better, and rarely less than 99.9 percent. Its high purity and its physical form make it a material highly suitable for addition to both ferrous and non-ferrous alloys. In the non-ferrous industry it is especially valuable as an addition to aluminum alloys. For manganese bronze and nickel-silver alloys it is advantageous for no correction need be made for other metals added with the manganese."

ACCEPTABILITY OF ELECTROLYTIC MANGANESE TO THE STEEL INDUSTRY [8]

For almost 2 years the U.S.B.M. has been conducting a program in cooperation with steel companies to determine the acceptability and possible advantages of electrolytic manganese as the form of manganese addition to steel instead of ferro-manganese normally used. Tests are in progress or have been completed at 34 different steel plants with full-scale commercial heats of steel. In no case has it been found impossible or even undesirable to use electrolytic manganese as the form of manganese addition to the steel.

In the case of stainless steel extensive tests have proven beyond question that electrolytic manganese has decided advantages over low-carbon ferro-manganese normally used. The advantages in this instance are due primarily to the high purity of electrolytic manganese, particularly with respect to phosphorus and carbon. Advantages also are due to the physical form of chips, which permits more convenient handling of a smaller weight, and quicker dissolution in the molten steel.

In electric furnace practice for low-alloy and plain carbon steels, both acid and basic, electrolytic manganese has proved by results to be entirely acceptable as the form of manganese addition having

the same advantages as with its use in the production of stainless steel.

In acid and in basic open-hearth steel practice, results of the tests to date indicate that larger additions of electrolytic manganese can be made satisfactorily to the ladle than can ferro-manganese, thus cutting the loss of manganese to the slag always present in furnace addition practice.

> "The results of full-scale production tests in steel plants prove beyond question that electrolytic manganese is acceptable as a manganese addition agent in the manufacture of most types of steel having definite advantages in stainless steel; in low-carbon steels, definite cost savings and improved quality of product; in medium-carbon steels improvement in quality has been indicated.
>
> "From the cost standpoint electrolytic manganese, even at its present small production and relatively high cost, is competing successfully with low-carbon ferro-manganese (the highest-priced grade of ferro-manganese). With the expected lowering of cost resulting from large-scale production, the electrolytic metal will compete with medium-carbon ferro-manganese and is expected to compete with standard high-carbon ferro-manganese (the lowest-priced grade of ferro-manganese) in some applications."

PREVIOUS INVESTIGATIONS

Much has been learned in recent years through investigation of the U. S. Bureau of Mines to aid our understanding of requirements necessary for treating some of the large bodies of low-grade ores of manganese, of which pyrolusite (MnO_2) in one of the most important minerals.

Treatment is necessarily specific in being suited to the region as well as to the variant character of manganese ores. The formation of manganous sulphate in solution is usually the first step in the treatment of the ores by hydrometallurgical extraction. The extraction treatment is, where feasible, preceded by suitable and systematic ore dressing to govern the favorable fineness for processes of leaching and agitation.

Manganese dioxide is insoluble in sulphuric acid but is readily acted upon by sulphur dioxide which dissolves the manganese as manganese sulphate. Sulphuric acid readily dissolves most other oxides of manganese other than the dioxide. Therefore the dissolution of manganese dioxide to form $MnSO_4$ in solution, can be carried out in one of two ways.

I. Preliminary roast the manganese dioxide (MnO_2) in a reducing atmosphere at a temperature of 500° to 550° C. At this temperature, the manganous oxide (MnO) formed is more stable and less subject to reoxidation

in air than if reduced at a higher temperature. At this temperature the iron in the ore is reduced to its most insoluble form, Fe_3O_4. Manganous oxide (MnO) is readily soluble in dilute H_2SO_4. This method is at present used by the sole commercial producer, The Electro-Manganese Corporation at Knoxville, Tennessee, which is now regularly producing approximately four tons of metallic manganese a day. A total of 8,647,250 pounds being produced from 1939 to January 1, 1945.

This practice of preliminary reduction roasting is also used by the United States Bureau of Mines in their new research laboratory at Boulder City, Nevada. Their pilot plant now producing approximately oneton of electrolytic manganese a day, with a total production of 500 short tons to January 1, 1945.

II. Leach the MnO_2 directly with SO_2 gas thus avoiding the preliminary roasting operation. An aqueous solution of SO_2 dissolves the higher oxides of manganese with formation of manganous dithionate (MnS_2O_6) and manganous sulphate ($MnSO_4$). By passing a controlled volume of air into the solution along with the SO_2, sulphuric acid will be produced which will dissolve any lower oxides present. SO_2 can be produced cheaply by burning sulphur or better if the situation permits by utilizing the SO_2 produced in

copper smelting. (The SO_2 content of convertor gases will range from 3.0 to 13.0 percent, roaster gases ranging from 4.0 to 9.0 percent) its use would result in the utilization of an obnoxious waste product with the recovery of manganese sulphate in solution.

From the resulting solution the following could be produced:

1. $MnSO_4$ for fertilizers could be produced by simple evaporation.
2. The leach solution after neutralization and evaporation to produce $MnSO_4$ salt which can be roasted in a rotary kiln to yield a calcine of manganese oxide and sulphur dioxide gas. The gas may be recovered and reused. The hot manganese oxide is nodulized to produce a product containing 65 percent or more manganese suitable to making a high grade ferro-manganese.
3. Under suitable conditions, metallic manganese can be electrolytically deposited from manganese sulphate solution, with or without simultaneous production of considerable manganese dioxide on the anodes.

As previously stated the high cost of treating the manganese mineral and the recent progress in development of a commercial method for the production of electrolytic manganese, favor its preparation if possible.

MONTANA'S POSITION IN NATIONAL PRODUCTION OF MANGANESE

Montana has to date been the nations leading producer of commercial grade manganese. Total production from 1838 - 1944 amounting to 1,419,924 short tons or 51 percent of the total United States production over the same period. According to N. B. Melcher - Mineral Yearbook 1944.[6]

> "Manganese ore in Montana comes from the Philipsburg district in Granite County and the Butte district in Silver Bow County. Since 1941 when operations were begun the nodulizing works of the A. C. M. Co. has been the nations leading producer of high-grade manganese raw material. During 1944 this operation produced 53 percent of the total United States output of manganese ore. The nodules averaged (natural) 60.61 Mn."

> "The second largest producer in the United States was the nodulizing works of the Domestic Manganese & Development Co. at Butte. Manganese oxide and carbonate ores from Philipsburg were treated, however it was discovered that flotation was more satisfactory using carbonate ores alone and the use of oxides was discontinued."

These ores could be treated by hydrometallurgy and with the states natural resources including hydro-electric power, produce a high grade electrolytic manganese. Increased use of electrolytic manganese in the ferrous field and the discovery of new uses during the war are expected to continue. Marked increase in the demand for the material during 1944 taxed the ability of the producers to supply sufficient metal.

LEACHING EXPERIMENTAL WORK

A portion of Philipsburg manganese oxide ore was obtained from the Domestic Manganese & Development Co. here in Butte. This was not a representative sample of the ore from the Philipsburg area, however it would suffice for our work.

Rock was crushed to -28 mesh and a representative sample taken and further ground to -80 mesh. All further work being done on portions of this sample which assayed 33.9 percent Mn.

Method of Making Tests:

All samples crushed to -80 mesh.

The sulphurous acid solution was prepared by passing SO_2 from a cylinder through distilled water than analized by the method given by Van Barneveld and Leaver.[7]

All tests made in sealed jars (somewhat over one-half full of air) and agitated on rolls at room temperature.

Percent recovery figured from strength of pregnant solution at end of leaching period.

All assays for manganese obtained by the Volhard method of analysis.

TEST NO. 1

It has been known for sometime that MnO_2 is soluble in sulphurous acid. The U. S. Bureau of Mines found:[3]

> "An excess of a 2 percent (by weight) solution of SO_2 in distilled water dissolved the manganese from the minerals in 15 minutes when crushed to -100 + 200 mesh, placed in stoppered bottles and agitated on rolls at 25° C."

However the character of manganese minerals varies greatly in different districts so the rates of dissolution in minerals from different sources may differ.

Therefore to confirm the statement of the U. S. B. M. and also to become familiar with the methods of testing, a 10 gram sample (-80 mesh) in an excess of a 1.6 percent (by weight) solution of SO_2, was agitated in a sealed jar at room temperature (22° C).

RESULT:

The sample was almost completely dissolved in 10 minutes and after 15 minutes the solution showed a recovery of 99.6 percent of the manganese. However no black MnO_2 was visible in the white silica residue, so it is believed the sample was completely dissolved, confirming previous investigations and also proving the ore contains no minerals of manganese which are insoluble in one of the two acids present (H_2SO_3 and

H_2SO_4). Although the leaching solution was meant to contain only H_2SO_3, small amounts of H_2SO_4 would be present by oxidation during agitation and by combination with any oxygen dissolved in the water when the SO_2 gas was introduced.

The feasibility of treating manganese ores by hydrometallurgy using SO_2 gas as a leaching agent and subsequent treatment of the solution for production of electrolytic manganese is considerably effected by the ability to reuse in the leaching cycle the spent electrolyte from the electrolytic cells. For every gram of electrolytic manganese deposited from a $MnSO_4$ solution, theoretically $\frac{98}{54.9}$ or 1.79 grams of sulfuric acid is produced in the anode compartment. In actual practice at the U. S. B. M. electrolytic manganese pilot plant [8]

> "The spent electrolyte contains 13 grams of manganese as $MnSO_4$, 130-135 grams $(NH_3)_2SO_4$ and 39-40 grams H_2SO_4; per liter."

Further, some sulphuric acid will be produced in introducing SO_2 gas into the leach solution. Therefore it seems desirable to determine the optimum leach for utilization of H_2SO_4 as compared with the amount of SO_2 required for dissolution.

TEST NO. 3

To determine the consumption of SO_2 in the dissolution of manganese, 1 cc of H_2SO_4 was added to the leach hoping to lessen the consumption of the SO_2 solution in the formation of insoluble sulphates.

Leaching Conditions:

Agitation - 1 hour at room temperature in sealed jars.

Strength of SO_2 solution - 16.3 gm. SO_2/liter

Volume of leach-constant at 101 cc.

Sample Wt. (gm)	H_2O Vol. (cc)	H_2SO_4 Vol. (cc)	Vol. SO_2 Sol'n (cc)	Mn. % Recov.
1.0000	100	1	0	1.1
1.0005	90	1	10	22.8
1.0020	80	1	20	44.5
1.0000	70	1	30	62.7
1.0003	60	1	40	79.6
1.0007	50	1	50	93.5
1.0010	45	1	55	100.0

Results of test: 0.3393 grams manganese required $55 \times 0.0163 = 0.8965$ grams SO_2.

$\frac{0.8965 \text{ gm } SO_2}{0.3393 \text{ gm Mn}} = 2.64$ grams SO_2/gm manganese leached.

Theoretically the consumption of SO_2 to form $MnSO_4$ would be 1.17/gms/gm Mn and 2.34 gm SO_2/gm Mn to form MnS_2O_6. The excess consumption obviously indicates the solution of other bases and formation of dithionate. The avoidance or control of the development of manganese dithionate requires the consideration of many chemical and mechanical factors.

There is a difference of opinion of the ability to control its formation. U. S. B. M. states:[9]

> "From the result of tests there is no practical method of preventing formation of dithionate by the use of excess H_2SO_4."
>
> "The consumption of Sulphur is independent of the rate or method of addition of H_2SO_4. The total S consumption per lb. Mn leached is the same in each case. The ratio of $SO_4^=$ to $S_2O_6^=$ is independent of the amount of H_2SO_4 and the manner in which it is introduced during the leach."

Contrary to this:[9]

> "If a sulphuric acid leaching does not precede the sulphur dioxide leach there is a tendency to produce dithionates."

There is also some question as to the effect of the temperature of the leach upon the formation of dithionate. According to E. A. Hersam:[10]

> "Reaction occurs between the aqueous solution of the gas and the manganese oxide in accordance with one or both of the following reactions:
>
> $$MnO_2 + SO_2 = MnSO_4 \qquad (1)$$
>
> $$MnO_2 + 2SO_2 = MnS_2O_6 \qquad (2)$$
>
> The treatment is required to be conducted at an elevated temperature, as with gases hot from the roasters. Reaction without this heating results in increasing the less desired effect indicated by reaction (2) above."

and according to J. H. Hunter:[11]

> "Manganous dithionate, MnS_2O_6, is formed by the action of sulphurous acid in the cold."

Contrary to this:[9]

> "Series of tests conducted by the U. S. B. M. indicates the dithionate is formed independent of the temperature of the leach."

TEST NO. 4

As shown by the previous test the consumption of SO_2 was 2.26 times the theoretical amount necessary for dissolution of manganese as $MnSO_4$. It is now necessary to determine the effectiveness of the degree of acidity of the solution in sulphuric acid with different strengths of sulphurous acid, attempting to improve the recovery of Mn, with same strength SO_2.

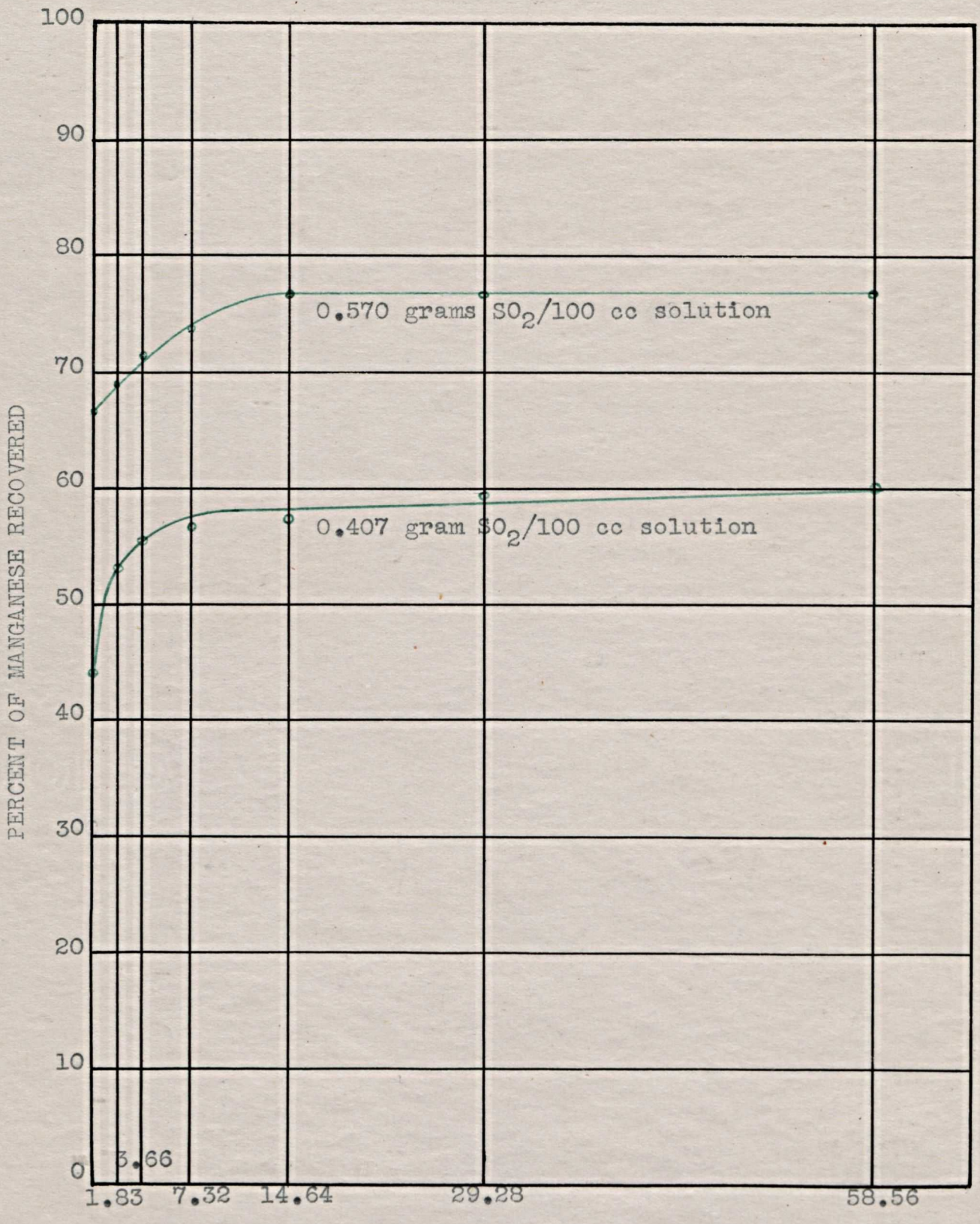
Leaching conditions:

Volume of solution kept constant at 100 cc.

Agitated for one hour at room temperature.

Strength of sulphurous acid kept constant at 25 cc of solution equivalent to 0.407 grams SO_2 or sufficient, theoretically to completely leach 0.348 grams of manganese or a 1.03 gram sample.

Sample Wt. (gm)	H_2O Vol. (cc)	Vol. SO_2 Sol'n (cc)	H_2SO_4 Vol. (cc)	Mn. % Recov.
1.0020	75	25	0	44.0
1.0022	74	25	1	51.5
1.0000	73	25	2	55.5
1.0010	71	25	4	56.5
1.0000	67	25	8	57.1
1.0010	59	25	16	59.5
1.0000	43	25	32	60.0
Strength of sulphurous acid kept constant at 35 cc of solution equivalent to 0.570 grams SO_2 or sufficient theoretically to leach 0.488 gm manganese or 1.44 grams of our sample.				
0.9997	65	35	0	66.5
1.0003	64	35	1	68.9
1.0000	63	35	2	71.6
1.0010	61	35	4	73.4
1.0012	57	35	8	76.6
1.0010	49	35	16	76.8
1.0005	33	35	32	76.8


100
90
80
70
60
50
40
30
20
10
0
PERCENT OF MANGANESE RECOVERED
0.570 grams SO_2/100 cc solution
0.407 gram SO_2/100 cc solution
3.66
1.83
7.32
14.64
29.28
58.56
Grams of H_2SO_4 per 100 cc of leach solution

Results of test:

The addition of sulphuric acid to the leach improved the recovery as indicated by the foregoing figures and graph. From the graph we may conclude that 14.64 grams (8 cc C. P.) sulphuric acid per 100 cc of solution would be the optimum acidity in H_2SO_4 for the ore in question. This amounts to a 15 percent (by wt.) H_2SO_4 solution before addition of SO_2 gas. Neglecting any small amount of H_2SO_4 formed by oxidation of the SO_2 in solution. This conforms with the results of Test No. 2.

In practice this strength of acid could be produced and maintained by the rate and quantity of air introduced into the leach with the SO_2 gas. The spent electrolyte from the electrolytic cells would contain approximately 40 grams acid per liter so an additional 100 grams $\pm$ would be needed to bring it up to this strength.

The addition of sulphuric acid aided in the recovery of manganese probably by dissolution of other bases present in the ore, thus reducing the consumption of SO_2. Whether the acid retarded the formation of dithionate or not was not determined and is open to question.

TEST NO. 5

The purpose of these tests was to determine if the increase in recovery, through the presence of acid in the leach solution, is consistent with different concentrations of SO_2 present and, assuming 15 percent H_2SO_4 optimum acidity, to determine the minimum amount of SO_2 needed for complete dissolution of the manganese.

Leaching conditions:

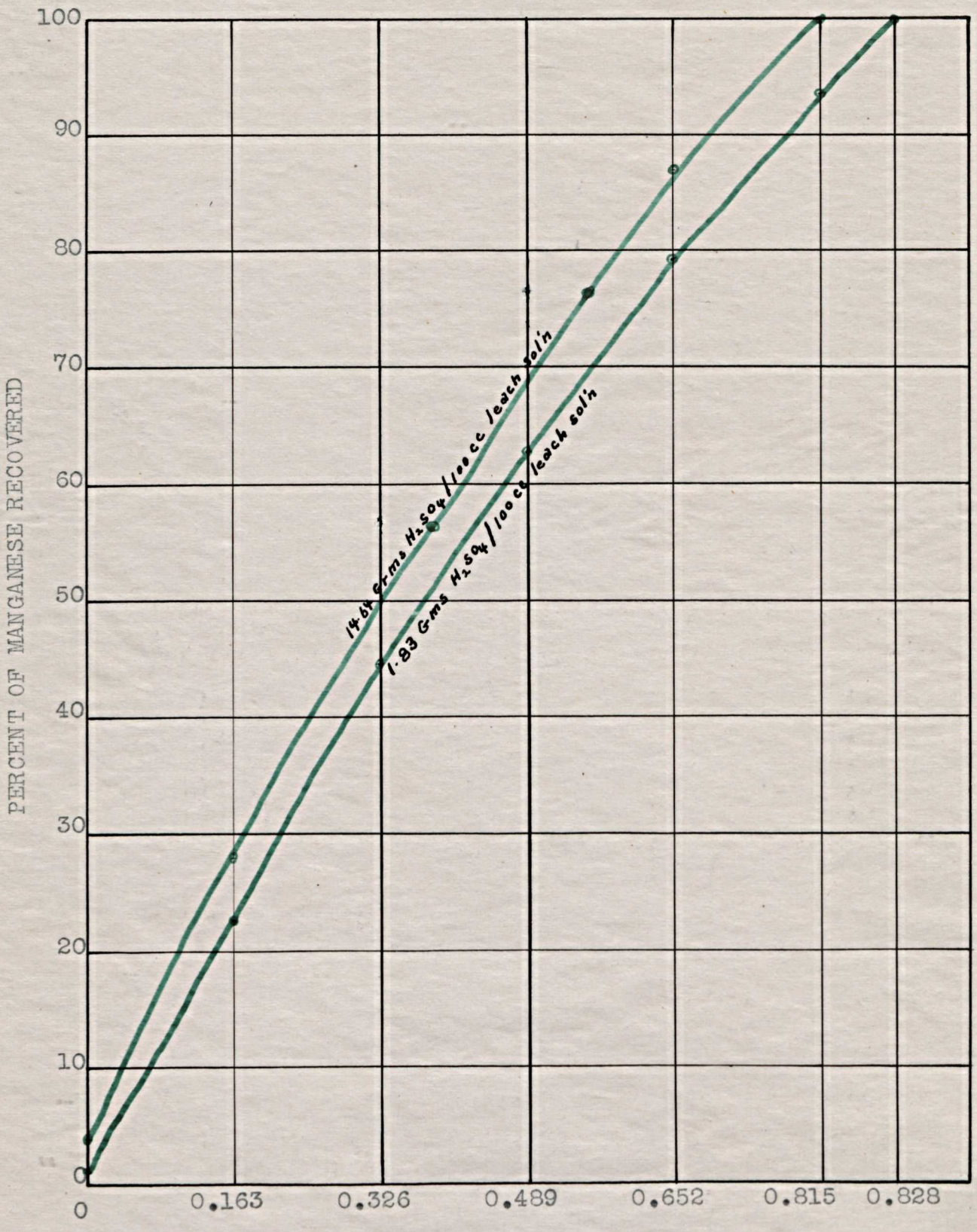
Agitated for 1 hour in sealed jars at room temperature.

Volume of solution constant at 100 cc.

Sample Wt. (gm)	H_2O Vol. (cc)	H_2SO_4 Vol. (cc)	Vol. SO_2 Sol'n (cc)	Mn. % Recov.
1.0000	92	8	0	3.8
1.0000	82	8	10	28.0
1.0000	67	8	25	57.1
1.0012	57	8	35	76.6
1.0015	52	8	40	86.8
1.0000	42	8	50	99.8

Results of test:

From the curve it appears the presence of the acid in the leach improves the recovery of manganese increasingly greater as the strength of the SO_2 solution becomes greater. Therefor in commercial practice where a 4-8 percent SO_2 leach solution would be used as compared to a maximum of 0.8 percent SO_2 solution used in testing the presence of the acid should help considerably. Perhaps with a stronger SO_2 leach solution a greater H_2SO_4 acidity than 15 percent would prove beneficial.

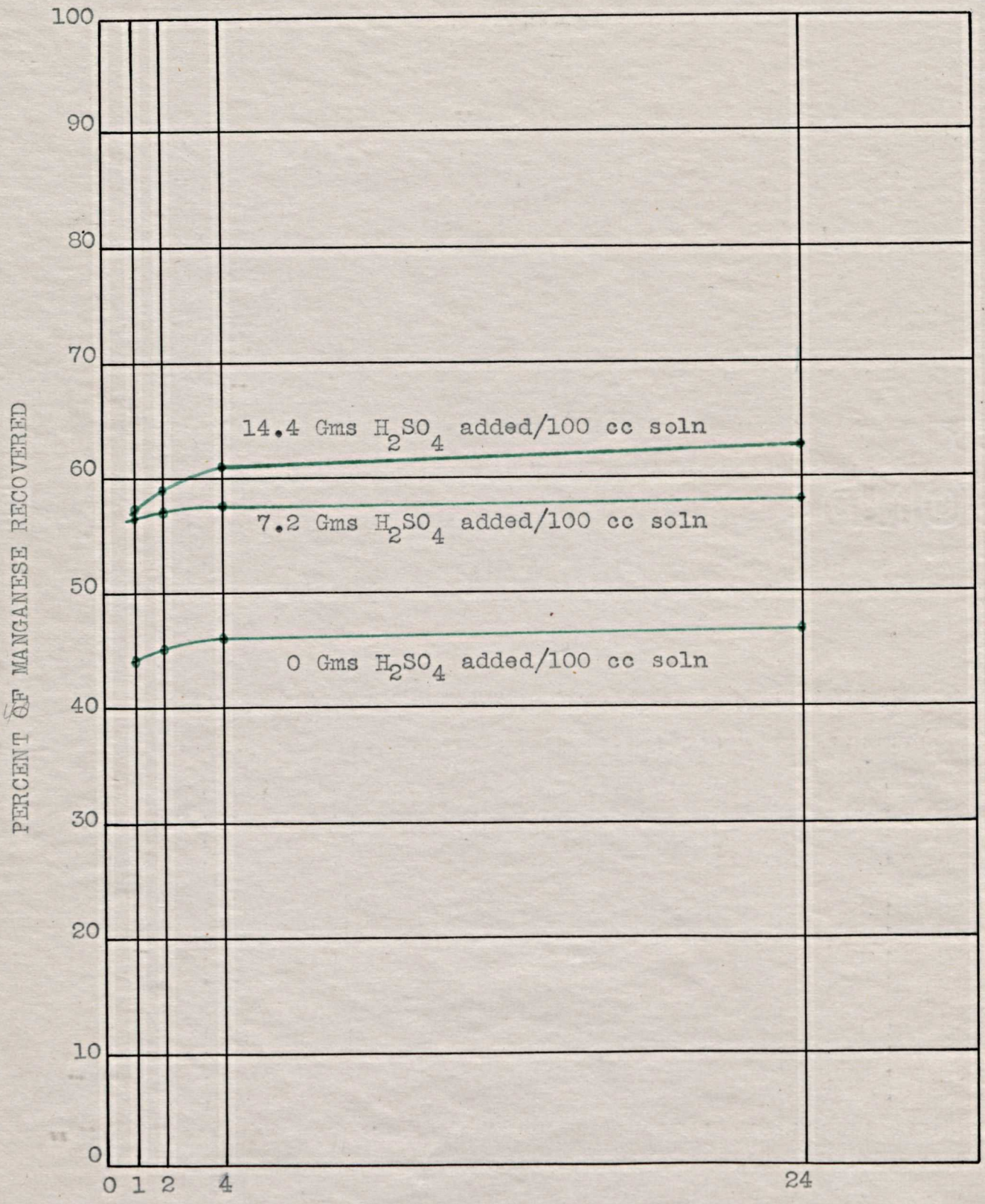

PERCENT OF MANGANESE RECOVERED
100
90
80
70
60
50
40
30
20
10
0
0
0.163
0.326
0.489
0.652
0.815
0.828
1.64 Grms H2SO4/100 cc leach sol'n
1.83 Grms H2SO4/100 cc leach sol'n
Grams SO2/100 cc Leach Sol./1 gram ore

TEST NO. 6

From previous tests it was found that with optimum acidity (15%) it required 50 cc of SO_2 solution or a total of 0.815 grams SO_2 for complete recovery of manganese from 1 gram of ore or 0.339 grams of manganese. Theoretically the consumption of SO_2 to form $MnSO_4$ should be 0.395 grams SO_2 per gram of ore. Therefore the efficiency of the SO_2 in leaching the MnO_2 being but 48.5 percent.

The following series of tests were performed to determine the necessary time of leach for optimum recovery, and effect of time of leach on different acidity.

Sample Wt.	H_2O Vol.(cc)	SO_2 Vol. Sol'n	H_2SO_4 Vol.(cc)	Time Hrs.	Mn. % Recov.
1.0020	75	25	0	1	44.0
1.0000	75	25	0	2	44.9
1.0005	75	25	0	4	45.9
1.0005	75	25	0	24	46.5
1.0010	71	25	4	1	56.5
1.0005	71	25	4	2	56.9
1.0005	71	25	4	4	57.5
1.0000	71	25	4	24	58.0
1.0000	67	25	8	1	57.1
0.9999	67	25	8	2	59.2
1.0020	67	25	8	4	60.9
0.9995	67	25	8	24	62.8


100
90
80
70
60
50
40
30
20
10
0
0 1 2 4 24
PERCENT OF MANGANESE RECOVERED
14.4 Gms H_2SO_4 added/100 cc soln
7.2 Gms H_2SO_4 added/100 cc soln
0 Gms H_2SO_4 added/100 cc soln
Time of Leach (hours)

Results of Test: The additional time of leaching did not improve the recovery to any reasonable degree. Although an additional time of agitation of 23 hours for the 15 percent acid solution improved the recovery by 5.7 percent, this would not be economically sound if the SO_2 reagent is cheap. In fact with an excess of a stronger SO_2 solution the 1 hour time could be cut down or if maintained perhaps a coarser grind would suffice.

CONCLUSIONS

1. The Philipsburg pyrolusite so far as represented by the sample can be satisfactorily leached with a high manganese recovery by the use of a dilute aqueous solution of H_2SO_3 formed by passing SO_2 gas into water.
2. The presence of sulphuric acid in the leach aids the recovery of manganese by giving a greater weight of manganese recovered per unit weight of SO_2 consumed. The optimum acidity in sulphuric acid for the weak SO_2 solution used being 15 percent (by weight). However results of tests indicate this figure should increase as the concentration of SO_2 in the leach solution became greater.
3. The high consumption of SO_2 indicates the formation of manganese dithionate (MnS_2O_6) and dissolution of other bases.
4. The use of SO_2 as a leaching agent for MnO_2 to form a marketable $MnSO_4$, or for further pyrometallurgical treatment to form an oxide sinter suitable for making a high grade ferromanganese, may be practical. However for subsequent electrolytic treatment for production of electrolytic manganese the SO_2 leaching may best serve not as a competitor but as an accessory process in conjunction with primary

roasting and subsequent leaching with sulphuric acid, thus compensating for the acid losses in a straight sulphuric acid leach. In present commercial practice this loss amounts to about 1/2 pound acid per pound of manganese produced due to mechanical loss and acid removed from the circuit as insoluble sulphates.

RECOMMENDATIONS

FOR FURTHER INVESTIGATION

1. Similar tests should be made to determine the effect of the temperature of the leach on the effectiveness of the various degrees of acidity of the solution in sulphuric and sulphurous acid.

2. Consumption of sulphuric acid in leaching should be determined before the SO_2 leach can be considered for further treatment in electrolytic deposition for the consumption should equal or exceed the amount of acid formed in the electrolytic cells.

3. Spent electrolyte contains approximately 135 grams of ammonium sulphate per liter. Tests should be made determining its effect upon the leaching cycle.

4. The control of the development of manganese dithionate, during extraction.

5. In practice other waste gases as N_2, CO_2, CO, in addition to the SO_2 entering the leach solution may introduce problems.

6. [10] "The close association of manganese oxide minerals with other components of the ore including iron, calcium, phosphorus, silicon, aluminum, and other elements requires the consideration, in practice of many chemical and mechanical factors; i. e. the selectivity of the solvent on the various desired and undesired minerals of the ore."

BIBLIOGRAPHY

1. Leith, C. K., Principles of Foreign Mineral Policy of the U. S., Min. & Met., January 1946.

2. Bulletins, 173, U. S. Bureau of Mines (1919)

3. Davis, E. W., Rept. of Inv., 3024, U. S. Bureau of Mines.

4. Dean, R. S., Electrolytic Manganese, Min. & Met. Vol. 22, No. 409, January 1941.

5. Dean, R. S., A. I. M. E. Tech. Paper, 1721, June 1944.

6. Melcher, N. B., Minerals Yearbook 1944.

7. Van Barneveld & Leaver, U. S. Bureau of Mines, Tech. Paper 312, Pg. 77.

8. Allen, G. L., U. S. Bureau of Mines, Rept. of Inv., 3815, June 1945.

9. Rep. of Inv., U. S. Bureau of Mines, 3649, July 1942.

10. Hersam, E. A., Liddell Handbook of Nonferrous Met., 1945, Pg. 575.

11. Hunger, J. H., A. I. M. E. Tech. Paper, 1717, Feb. 1944.

ACKNOWLEDGEMENT

The writer wishes to express his appreciation and gratitude to Professor J. P. Spielman, Head of the Department of Metallurgy at the Montana School of Mines, for his assistance, advice, and guidance on the work represented by this Thesis, and under whose supervision it was conducted.